PHOTON-ECHO RELAXATION IN MOLECULAR MIXED CRYSTALS

AARTSMA, TJ; WIERSMA, DA; Aartsma, Thijs J.

Published in:
Chemical Physics Letters

DOI:
10.1016/0009-2614(76)80667-7

Publication date:
1976

PHOTON-ECHO RELAXATION IN MOLECULAR MIXED CRYSTALS

Thijs J. AARTSMA and Douwe A. WIERSMA
Laboratory for Physical Chemistry, University of Groningen, Groningen, The Netherlands

Received 3 June 1976

The results of a photon-echo relaxation study on the lowest $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of tetracene and pentacene in a *p*-terphenyl host crystal are reported. The photon-echo decay times were measured at 1.37 K and found to be 8.2 ± 1 ns for tetracene and 13.8 ± 0.5 ns for pentacene. These relaxation times correspond to *homogeneous* linewidths of 19.4 and 11.5 MHz respectively and are over a factor of 10^3 smaller than the observed inhomogeneous linewidths in the optical absorption spectrum. Temperature dependent photon-echo intensity measurements further show that, below 3.5 K, optical relaxation is due to an Orbach process with a presumably pseudolocalized phonon state. The resonant phonon frequency was measured to be 8.1 ± 1 cm^{-1} for tetracene and 21.2 ± 0.5 cm^{-1} for pentacene.

1. Introduction

The first reports of photon-echo [1] and self-induced transparency [2] measurements on ruby already clearly demonstrated the potential of coherent optical phenomena to the study of relaxation effects of optical transitions.

Progress in this field however has been rather slow in the past decade mainly because of the fixed frequency limitation of the early lasers.

With the advent of the tunable dye lasers, optical relaxation studies have become possible throughout the whole of the visible spectrum and some very recent experiments using both pulsed [3] or cw [4] dye lasers witness of these new possibilities.

In a recent note [5] we reported the first successful photon-echo experiment on a molecular mixed crystal using a pulsed tunable dye laser.

In this paper we present the results of new photon-echo experiments performed on the lowest short-axis polarized transitions of tetracene and pentacene in a *p*-terphenyl host crystal.

The photon-echo decay times were measured and found to correspond to homogeneous linewidths of ca. 15 MHz at 1.3 K in these mixed crystals.

The temperature dependence of the photon-echo intensity further shows that below 3.5 K the origin homogeneous linewidth in these solids is only determined by an Orbach relaxation process with a presumably pseudolocalized phonon state. The resonant phonon frequency is found to be strongly dependend on the guest molecule but shows little variation among the different sites in the *p*-terphenyl crystal.

2. Experimental

p-terphenyl was purified by zone refining (60 passes) and single crystals doped with tetracene and pentacene (10^{-5}–10^{-6} molar) were grown from a temperature controlled Bridgman furnace. The crystals were cleaved parallel to the *ab* cleavage plane with a sharp razor blade and only crystals with good optical quality were selected and used. This is necessary in order to minimize scattering from the surfaces.

p-terphenyl crystals are monoclinic ($P2_1/a$) at room temperature with two molecules in the unit cell [6] and the lowest spin-allowed transition ($^1B_{2u} \leftarrow {}^1A_{1g}$) of tetracene [7] and pentacene [8] in this host crystal is *b*-polarized. The crystals were therefore oriented with the *b*-axis parallel to the polarization direction of the exciting laser pulses.

In fig. 1 a scheme of the experimental set-up is given. As excitation source a Molelectron DL 200 dye laser, pumped by a 1 MW nitrogen laser at a repetition rate of 10 Hz, is used. The dye laser, equipped with an

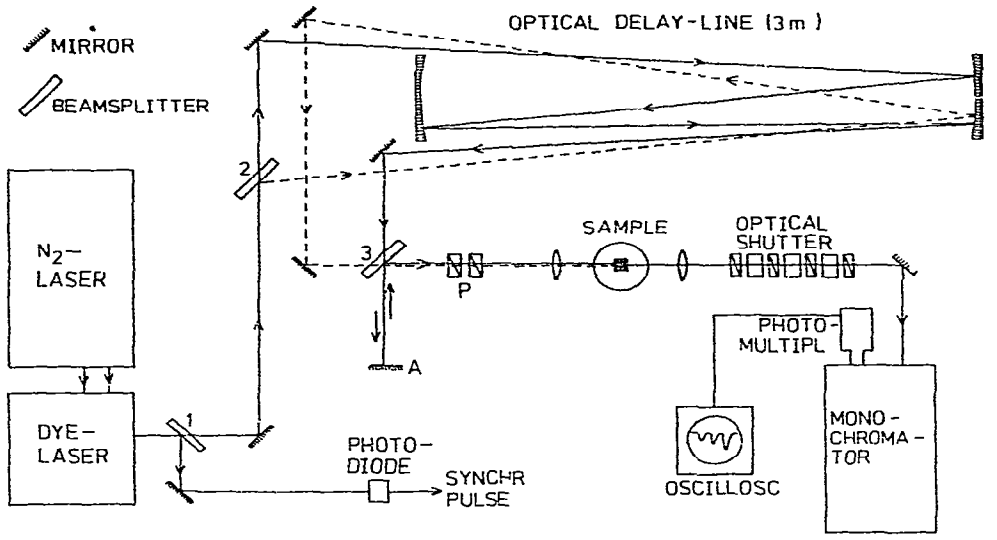

Fig. 1. Schematical representation of the experimental photon-echo set-up. Details are discussed in the experimental section.

intra-cavity polarizer, has an output pulse of 5 ns duration and a bandwidth of 0.4 cm^{-1}. Its maximum obtainable output power was 100–200 kW per pulse, of which only a fraction was needed in the experiments. Occasionally an intracavity etalon was inserted in the dye laser, but we never obtained a significant gain of echo-intensity versus exciting laser pulses intensity.

The two pulses, needed for the photon-echo experiment were generated by a beamsplitter 2 (30% reflectivity) and then delayed with respect to each other by an optical delay line. The delay line is constructed as a White-cell [9] with mirrors (Perkin Elmer Corporation) of 1.5 m focal length and 99.9% minimum reflectivity between 4200 and 6400 Å. In order to keep the divergence of the two beams identical both were passed through the delay line.

For measuring relaxation times we introduced an extra mirror A in the set-up. This mirror could be translated over a distance of one meter which corresponds to a maximum delay of 6.67 ns. The difference in divergence, caused by this extra delay, was minimized by usage of a telescope in the output beam of the dye-laser. The delayed pulse is then passed twice through beamsplitter 3 (50% reflectivity), of which only the second reflected part is used to excite the sample. The transmitted part returns into the dye laser, but no feedback pulses were observed. The final intensity ratio of the exciting laser pulses in this mode of operation was about one.

Spatial overlap of the two beams is obtained by adjustment of beamsplitter 3. The echo intensity was found to be extremely sensitive for minor rotations of this element. The intensity of the exciting pulses was optimized for maximum intense echoes by two polarizers P, which were oriented such, that the output polarization remained fixed.

The sample was contained in a temperature variable liquid helium cryostat (Oxford Instruments) with a stability and a reproducibility better than 0.01 K between 1.2 and 4.2 K. The absolute temperature reading in this temperature range is estimated to be within 0.03 K.

A fast optical shutter, consisting of three Pockell's cells in series (PC12KD, Electro Optics Development), was used to attenuate the exciting laser pulses prior to detection. This system, with a measured risetime of 1.5 ns and a specified attenuation factor of 10^9, is only switched into transmission for 10 ns during passage of the echo.

The use of a monochromator (5 Å bandwidth) prove essential, as otherwise the photon-echo is completely obscured by incoherent, nonresonant fluorescence to vibrational levels of the ground state.

The echo was detected with a Philips 150 UVP photomultiplier and displayed on a 454 Tektronix oscilloscope. Finally a PAR boxcar integrator with a digital storage option was used for time resolved intensity measurements.

3. Results

3.1. Photon-echo excitation spectrum

Fig. 2A shows the fluorescence excitation spectrum at 1.3 K of the origin of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition for two sites of pentacene in *p*-terphenyl at 16882 and 16887 cm^{-1}. The spectrum was obtained by slowly scanning the laser through the absorption region, while monitoring the fluorescence intensity at 6380 Å (5 Å band width) with a boxcar integrator. Fig. 2B shows the same scan, but now with resonant detection of the echo-intensity.

The lines in the photon-echo excitation spectrum are found to be sharpened (fwhm) by a factor of 0.77 and 0.69 respectively with regard to the absorption spectrum. These values are in agreement with the expected sharpening through the N^2-dependence of the echo-intensity (N is the number of excited molecules) by a factor of 0.71 for a gaussian line shape. The relaxation time of the photon echo thus is constant over the inhomogeneous linewidth.

Comparing further the intensity ratio of the lines in the photon-echo excitation spectrum with that of the absorption spectrum we conclude that the relaxation times of the two sites are almost identical. A similar behaviour is observed for the two sites of tetracene in *p*-terphenyl with origins at 20274 and 20277 cm^{-1} [10]. These observations are in contrast with the case of pyrene in biphenyl, where the different sites have markedly different photon-echo relaxation times [5].

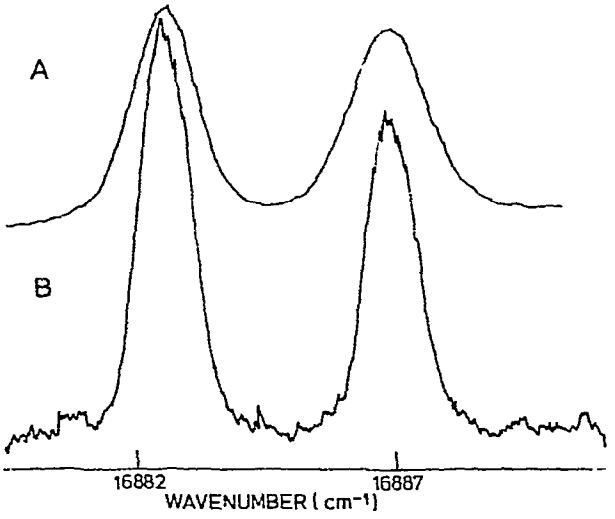

Fig. 2. Fluorescence excitation spectrum (A) and photon-echo excitation-spectrum (B) of the origin region of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of pentacene in *p*-terphenyl at 1.3 K.

3.2. Photon-echo lifetime

The echo-intensity as a function of exciting pulse separation for tetracene and pentacene was measured at 1.37 K for the energetically lowest sites by varying the position of mirror A. The results are given in fig. 3, showing an exponential decay of the echo intensity with increasing pulse separation:

$$I(t) = I(0)\,e^{-2t/T_2} ,$$

where t is the time interval between the first excitation pulse and the echo and T_2 the transverse relaxation time in the optical analog of the Bloch equations [11]. We found T_2 to be 16.4 ± 2 ns for tetracene and 27.6 ± 1 ns for pentacene. These relaxation times correspond to *homogeneous* linewidths $(\pi T_2)^{-1}$ of 19.4 and 11.5 MHz respectively and are over a factor 10^3 smaller than the observed inhomogeneous linewidths in the optical absorption spectrum. The lifetime T_2 of the photon-echo is determined by

$$1/T_2 = 1/T_2^* + 1/2T_1 ,$$

where T_1 is the fluorescence lifetime and T_2^* the (coherence) lifetime associated with phase-destructive events [12].

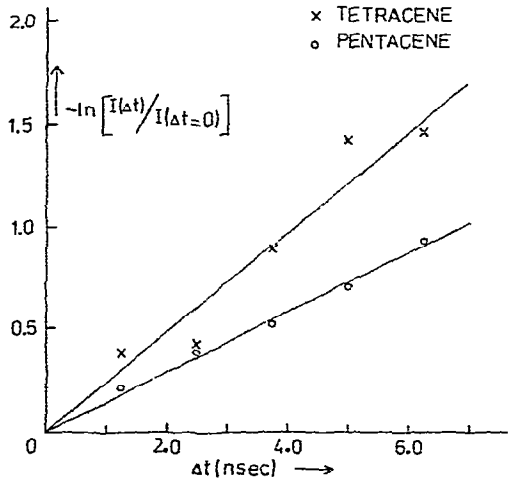

Fig. 3. A logarithmic plot of the relative echo-intensity at 1.37 K as a function of an extra delay between the exciting laserpulses. $\Delta t = 0$ corresponds to a 20 ns separation between the exciting pulses.

We have measured a T_1 of 32 ± 1 ns for tetracene and 39 ± 1 ns for pentacene, both in a *p*-terphenyl host crystal at 1.3 K‡. We then calculate a "coherence" lifetime T_2^* for the 16882 cm^{-1} site of pentacene of 44 ± 3 ns and for the 20274 cm^{-1} site of tetracene 22 ± 4 ns. These coherence lifetimes are typically a factor of five shorter than those found for inorganic mixed crystals [1,3,14,15].

3.3. Temperature dependence of the echo

The temperature dependence of the photon-echo intensity was measured between 1.2 and 4.2 K and the results are given in fig. 4. It turns out that the results can be very well fitted to an echo decay curve of the following form:

$$I(T) = I(0) \exp[-2t/T_2^*(T)] ,$$

where

$$[T_2^*(T)]^{-1} = [T_2^*(0)]^{-1} + (k_\infty)^{-1} \exp(-\Delta E/kT) .$$

$I(T)$ is the echo-intensity at temperature T (K) and t, being 40 ns, is the time interval between the echo and the first excitation pulse.

The solid curves in fig. 4 were calculated on basis of this relaxation behaviour using the following set of parameters. For tetracene: $T_2^*(0) = 22 \pm 4$ ns, $k_\infty = 78$ ps and $\Delta E = 8.1 \pm 1$ cm^{-1} and for pentacene $T_2^*(0) = 44 \pm 3$ ns, $k_\infty = 22.4$ ps and $\Delta E = 21.2 \pm 0.5$ cm^{-1}. We have also performed measurements on two other sites at 16887 and 16947 cm^{-1} of pentacene which show a similar temperature dependence of the photon-echo intensity with slightly different parameters; e.g. for both sites $\Delta E = 18.7 \pm 1$ cm^{-1}.

‡ We note that the fluorescence lifetimes of tetracene and pentacene reported here are a factor of four longer than those obtained from gas phase measurements [13].

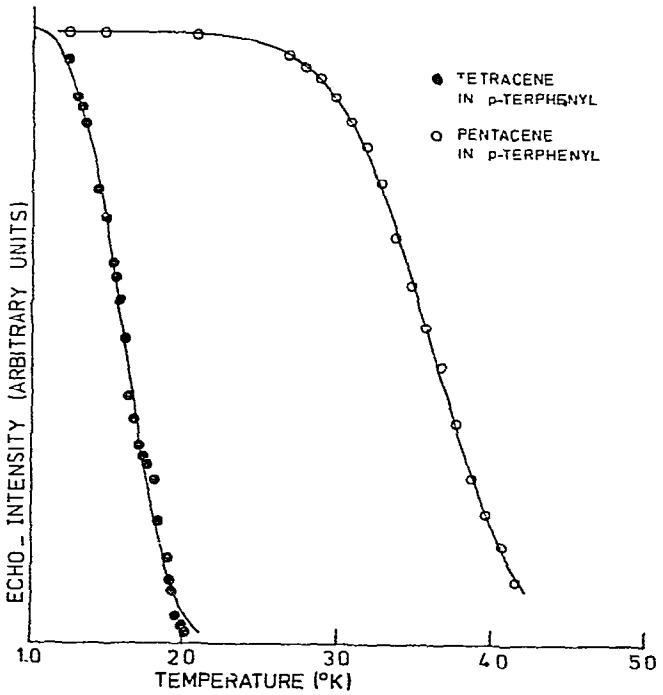

Fig. 4. Temperature dependence of the echo-intensity for the 20274 cm^{-1} site of tetracene and the 16882 cm^{-1} site of pentacene in *p*-terphenyl. Theoretical curves are shown with $\Delta E = 8.1 \pm 1$ cm^{-1}, $k_\infty = 76$ ps for tetracene and $\Delta E = 21.2 \pm 0.5$ cm^{-1}, $k_\infty = 22.4$ ps for pentacene. The exciting pulse separation in these experiments was 20 ns.

4. Discussion and conclusion

Our results show that even at 1.2 K the photon-echo decay time ($\frac{1}{2}T_2$) is not identical to T_1 but at least a factor of three shorter. This indicates that even at this temperature not all relaxation processes have been frozen out. The assignment of the remaining process(es), the decay rate of which is expressed by $[T_2^*(0)]^{-1}$, however is presently not clear. The fact however that $T_2^*(0)$ is markedly different for tetracene and pentacene encourages further experiments to clarify its meaning.

The temperature-dependent part of T_2^* on the contrar is directly physically interpretable. Its exponential form shows that the excited state coherence below 4.2 K is lost through an Orbach relaxation process. From the measured activation energies (ΔE) one must conclude that the intermediate level involved is a phonon state. In order to be effective in the relaxation process this phonon state must have a large amplitude at the guest site. Such phonons are known as pseudolocalized or resonance modes [16] and are also known to be optically accessible [17]. It is interesting to note that in the optical absorption spectrum of tetracene in *p*-terphenyl [10] one indeed observes a phonon side-band at 7 cm^{-1} from the zero-phonon line. This phonon frequency is, within the error limits, identical to the measured 8.2 ± 1 cm^{-1} activation energy of the Orbach relaxation process.

However in the absorption spectrum of pentacene

in a *p*-terphenyl mixed crystal the phonon sideband structure is broad and structureless and no pronounced phonon absorption at 21 cm^{-1} [18] is observed. Nevertheless it is quite remarkable that 21 cm^{-1} is well beyond the onset of the phonon sideband absorption spectrum in this mixed crystal system. This point certainly deserves further investigation but chances are that photon-echo experiments will enable us to identify in a broad and structureless phonon absorption region the underlying resonance modes.

Finally we need mention here the recent work of Burke and Small [19] who studied the temperature dependence of the linewidth and line-position of the $^1B_1 \leftarrow {}^1A_1$ transition of 2-phenyl-1-monoazaazulene in *p*-terphenyl. They find in the temperature range between 10 and 30 K that a Raman process (T^7 temperature dependence for the homogeneous linewidth) accounts for the observed optical linewidths. It would be interesting to study, with the photon-echo technique, the homogeneous linewidths in this mixed crystal system below 10 K to establish whether or not the Raman relaxation process at low temperature is superseded by an Orbach relaxation process.

Concluding we would say that the experiments reported in this paper, show that coherent optical studies of molecular crystals may add substantially to our knowledge of relaxation phenomena in these materials.

Acknowledgement

We are indebted to the Netherlands Foundation for Chemical Research (S.O.N.) for generous financial support of this investigation and to W.H. Hesselink for assistance in some of the experiments.

References

[1] N.A. Kurnit, I.D. Abella and S.R. Hartmann, Phys. Rev. Letters 13 (1964) 567; Phys. Rev. 141 (1965) 391.
[2] S.L. McCall and E.L. Hahn, Phys. Rev. 183 (1969) 457.
[3] N. Takeuchi and A. Szabo, Phys. Letters 50A (1974) 361.
[4] R.G. Brewer and A.Z. Genack, Phys. Rev. Letters 36 (1976) 959.
[5] T.J. Aartsma and D.A. Wiersma, Phys. Rev. Letters (June 7, 1976), to be published.
[6] L.W. Pickett, Proc. Roy. Soc. 142 (1933) 333.
[7] J.W. Sidman, J. Chem. Phys. 25 (1956) 122.
[8] J.H. Meyling and D.A. Wiersma, Chem. Phys. Letters 20 (1973) 383.
[9] J.U. White, J. Opt. Soc. Am. 32 (1942) 285.
[10] N.J. Kruse and G.J. Small, J. Chem. Phys. 56 (1972) 2985.
[11] F. Bloch, Phys. Rev. 70 (1946) 460.
[12] A.C.G. Mitchell and M.W. Zemansky, Resonance radiation and excited atoms (Cambridge Univ. Press, London, 1934).
[13] S. Okajima and E.C. Lim, Chem. Phys. Letters 37 (1976) 403.
[14] S. Chandra, N. Takeuchi and S.R. Hartmann, Phys. Letters 41A (1972) 91.
[15] N. Takeuchi, S. Chandra, Y.C. Chen and S.R. Hartmann, Phys. Letters 46A (1973) 97.
[16] P. Brout and V.M. Visscher, Phys. Rev. Letters 9 (1962) 54.
[17] R.M. Hochstrasser and P.N. Prasad, J. Chem. Phys. 56 (1972) 2814.
[18] T.J. Aartsma, W.H. Hesselink and D.A. Wiersma, unpublished results.
[19] F.P. Burke and G.J. Small, Chem. Phys. 5 (1974) 198.